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REPORT DOCUMENTATION PAGE				
1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS This document has been approved for public release and sale; its distribution is unlimited.		
2a. SECURITY CLASSIFICATION AUTHORITY SEP 27 1991		3. DISTRIBUTION/AVAILABILITY OF REPORT Unlimited Distribution		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 1991K-12		7a. NAME OF MONITORING ORGANIZATION ONR		
6a. NAME OF PERFORMING ORGANIZATION Kent State University		7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy St. Arlington, VA 22217-5000		
6c. ADDRESS (City, State, and ZIP Code) Kent State University Depts. of Chemistry & Physics and Liquid Crystal Institute, Kent, OH 44242-0001		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION DARPA		8b. OFFICE SYMBOL (if applicable)		
8c. ADDRESS (City, State, and ZIP Code) 3701 N. Fairfax Dr. Arlington, VA 22203-1714		10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
		WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) "Characterization of Polymer Dispersed Liquid Crystal Shutters by UV and IR Absorption Spectroscopy"				
12. PERSONAL AUTHOR(S) J.L. West and R. Ondris-Crawford				
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 6/30/90 TO 5/31/91		14. DATE OF REPORT (Year, Month, Day) 5/31/91
15. PAGE COUNT				
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
			Dichroic dyes;	
			polymer dispersed liquid crystal shutters	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)				
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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL J.W. Doane			22b. TELEPHONE (Include Area Code) (216)672-2654	
			22c. OFFICE SYMBOL	

OFFICE OF NAVAL RESEARCH

GRANT NO.: N00014-86K-0766

R&T Code: a40000df(Subcontract)

TECHNICAL REPORT NO. 1991K-12

"Characterization of Polymer Dispersed Liquid Crystal
Shutters by UV and IR Absorption Spectroscopy"

by

J.L. West and R. Ondris-Crawford

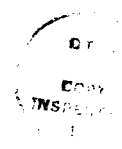
To Appear
J. Appl. Phys., Oct. 1991

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May 31, 1991

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91-11708

CHARACTERIZATION OF POLYMER DISPERSED LIQUID CRYSTAL SHUTTERS BY ULTRAVIOLET / VISIBLE AND INFRARED ABSORPTION SPECTROSCOPY

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ABSTRACT

Incorporation of dichroic dyes substantially improve the contrast of polymer dispersed liquid crystal (PDLC) shutters. The efficiency of dichroic dyes in a PDLC shutter depends on the scattering efficiency of the film, the dichroic ratio of the dye, the order parameter of the dye in the liquid crystal, and the fraction of dye dissolved in the droplets. Ultraviolet / visible (UV/VIS) spectroscopy can be effectively used to determine the scattering efficiency of PDLC films, and the distribution of dichroic dye dissolved in the liquid crystal droplets. To achieve high contrast the dichroic dye must be segregated in the droplet. We show that the segregation of dye in the PDLC droplets is dependent on the type of dye used and ranges from 19% to 100%. The scattering efficiency of the PDLC shutter provides insight into the effect of the dichroic dye on the contrast of the film. Production of a black PDLC shutter requires a mixture of several dichroic dyes. By careful consideration of the relative amounts of the components of the dye mixture, a black PDLC shutter can be constructed with a uniform contrast over the entire visible region. The dichroic absorption in the infrared of the liquid crystal used to make a PDLC can be analyzed in a manner analagous to the dichroic dye to determine the fraction of liquid crystal phase separated in droplets and dissolved in the polymer binder.

I. INTRODUCTION

Polymer dispersed liquid crystals (PDLC) are a new class of electro-optic material with a wide variety of applications ranging from architectural glass to active matrix color projection TVs¹⁻⁵. PDLCs are composites of low molecular weight liquid crystal droplets dispersed in a solid polymer binder sandwiched between two transparent, conducting electrodes.⁶ PDLCs usually have a bipolar director configuration.^{7,8} Figure 1 shows the bipolar droplet resulting from tangential alignment at the droplet surface. In the absence of an electric field (OFF state), the symmetry axes of the bipolar droplets are randomly oriented, and in general the refractive index of the liquid crystal droplet is mismatched with that of the polymer, resulting in an opaque appearance. In the presence of an electric field (ON state), the director orientation rotates to align the droplet director with the field. In the ON state, the refractive indices of the polymer binder and droplet are matched and the film is transparent.^{1,4} We have incorporated dichroic dyes into PDLC materials and determined, via UV/VIS spectroscopy, the fraction of dye that remains in the droplet after phase separation.

PDLC materials are formed by phase separation of low molecular weight liquid crystal from a homogeneous solution with a prepolymer or polymer. Several phase separation techniques are used to achieve uniform droplet sizes.⁹ It is possible to prepare uniform droplet sizes as large as 40 μm and as small as 0.01 μm .¹⁰ In this study we made PDLCs with droplet sizes ranging between 1 and 2 μm because this size maximizes light scattering in the OFF state and optimizes contrast for display applications.

Colored PDLCs are formed by incorporating dyes in the PDLC material. Unlike low molecular weight guest-host systems,¹¹ isotropic dyes can be used.^{12,13} The color contrast of the PDLC film containing an isotropic dye is a consequence of the increased path of the light passing through the film in the opaque relative to the

transparent state. Therefore, the change in absorbance is a direct measure of the scattering efficiency of the film. Recently, Drzaic et al.¹⁴ reported high brightness, high contrast color reflective mode displays by using a dichroic dye in NCAP films. The intrinsic optical order parameter is related to the performance of the NCAP film based on the orientation of the nematic director in the film.

Dichroic dyes employed in PDLC films produce higher contrast than isotropic dyes.¹⁵ The orientation of the elongated dye molecule is governed by the nematic director configuration inside the droplet as illustrated in Fig. 1. Therefore, the dye absorbance is modulated by the alignment of the nematic director with an external field. In the OFF state, we assume random orientation from droplet to droplet of the symmetry axes of the bipolar droplets resulting in random orientation of the dye molecules. The extinction coefficient is therefore averaged over all droplets and is equal to the isotropic extinction coefficient of the dye. In the ON state, the droplet director and the dichroic dye molecules dissolved in the droplet are aligned normal to the surface of the film and the dye extinction coefficient is equal to the perpendicular extinction coefficient. Dichroic dye that remains dissolved in the polymer binder will be unaffected by the external field and remain randomly oriented. Therefore, only the dye dissolved in the nematic droplet will exhibit dichroic properties and enhance the contrast of the film. Using the dichroic extinction coefficients of the dye and the absorption of the PDLC films in the ON and OFF states, we have determined the distribution of the dye between the polymer binder and the liquid crystal droplets of the PDLC.¹⁵

PDLC shutters have also been tailored for operation in the infrared (IR). This requires selection of liquid crystals,^{16,17} polymers and substrates with low IR absorption. Also the ordinary refractive index of the liquid crystal must be matched with the polymer in the IR and the liquid crystal droplet size must be on the order of the wavelength of the IR radiation to be modulated.^{18,19} The dichroic absorption of

the liquid crystal, the absorption of the polymer and the light scattering of the resulting PDLC have been studied in the IR using fourier transform infrared (FTIR) spectrometry.²⁰ Using the dichroic absorption of the cyano stretch of the cyanobiphenyl liquid crystal mixture E7 we have determined, in a manner analogous to the dichroic dyes, the distribution of the liquid crystal between the polymer binder and the liquid crystal droplets.

In section II, a brief account of the principle of absorbance calculations is presented, emphasizing the direct determination of the fraction of dye remaining in the droplet after phase separation. The experimental details of the sample preparation are given in Section III, and the empirical measurements using the UV/VIS spectrometer are discussed in Section IV. Section V is devoted to the description of the results for various dye compounds. Concluding remarks are given in Section VI.

II. THEORY OF ABSORPTION MEASUREMENTS

The absorbance, A , of a dichroic dye contained in a PDLC shutter is the sum of the absorbance of the dichroic dye dissolved in the polymer binder and nematic droplets and is given by the expression:

$$A = A_{\text{droplet}} + A_{\text{binder}} \quad (1)$$

The linear relationship between absorbance and the path length at a fixed concentration of absorbing substance is generalized by Beer's Law²¹:

$$A = \epsilon c l \quad (2)$$

where ϵ is the dye extinction coefficient, c is the dye concentration, and l is the path length of light. Because of the anisotropy of the dye molecules dissolved in the liquid crystal droplet, the extinction coefficient is defined for various orientations of the nematic director where ϵ_{\perp} is the extinction coefficient measured perpendicular to

the nematic director, ϵ_{\parallel} is the extinction coefficient measured parallel to the nematic director, and ϵ_i is the isotropic extinction coefficient.

The isotropic extinction coefficient can be defined as a weighted average over the parallel and perpendicular components given by the following relation:

$$\epsilon_i = \frac{2\epsilon_{\perp} + \epsilon_{\parallel}}{3} \quad (3)$$

The measured dichroic ratio, R , of the dissolved dye in the liquid crystal is defined as:

$$R = \epsilon_{\perp} / \epsilon_{\parallel} \quad (4)$$

In the OFF state, the symmetry axes of the bipolar droplets vary randomly from droplet to droplet and the average extinction coefficient of a collection of droplets is ϵ_i . The path length in the OFF state can be defined by the relation:

$$l = \alpha d \quad (5)$$

where d is the thickness of the PDLC film and α is defined as the scattering efficiency. The absorption in the OFF state can then be expressed as:¹⁴

$$A_{OFF} = \epsilon_{\parallel} X \alpha d + \epsilon_i (1 - X) \alpha d \quad (6)$$

where X is the fraction of dye in the nematic droplet and $1-X$ is the fraction of dye dissolved in the polymer binder after the phase separation process. We assume the extinction coefficient of the dye is the same in a liquid crystal and polymer solvent. Equation 6 simplifies to:

$$A_{OFF} = \epsilon_i \alpha d \quad (7)$$

Equation 7 allows the scattering efficiency to be determined from the measured A_{OFF} .

In the ON state, the droplet directors are aligned perpendicular to the surface of the film, and therefore the dye in the droplet has the perpendicular extinction

coefficient and the dye in the binder has the isotropic extinction coefficient. In the ON state, the path length is just the thickness of the film. The absorption in the ON state is thus given by the following expression:

$$A_{ON} = \epsilon_{\perp} Xcd + \epsilon_i (1-X)cd \quad (8)$$

The fraction of dye in the droplet, X , is calculated directly from Eq. (8) using the measured ON state absorbance and the measured extinction coefficients of the dichroic dye.

Using the dichroic absorption in the IR of the cyano stretch of E7 allows similar analysis of the dichroic IR absorption of the liquid crystal in a PDLC to be used to determine the distribution of the liquid crystal in the film and the scattering efficiency at IR wavelengths.

III. SAMPLE PREPARATION

PDLC shutters were formed by polymerization induced phase separation. Four dichroic dyes supplied by Hoffman La Roche were used in this study: a yellow dye (Y2), two red dyes (R4) and (R5), and one blue dye (B3). The dyes were dissolved in the eutectic liquid crystal mixture E7 (EM Chemicals) to form a 1% by weight solution. We used an epoxy system having a refractive index matched with the ordinary refractive index of the liquid crystal to obtain maximum transmission in the ON state. This is a three component epoxy system consisting of WC97, the triglycidylether of trimethylolpropane (Wilmington Chemicals), and Epon 828, the reaction product of epichlorohydrin and bisphenol A (Miller Stephenson) as the epoxy resins, and Capcure 3-800, a trifunctional mercaptan terminated liquid polymer (Miller Stephenson), as the cure agent. The components were thoroughly mixed with the liquid crystal according to the following weight ratios: E7 + dye (35%), Capcure (37%), Epon 828 (10%), and WC97 (18%). The resulting mixture was

stirred to form a homogeneous solution, and pressed between two glass substrates with transparent, conducting electrodes. Film thickness was controlled using 18 μm glass spacers. The samples were then cured in an 80°C oven for at least 4 hours resulting in polymerization, droplet formation and growth, polymer gelation, and final cure.

Aligned, low molecular weight dichroic cells were constructed to measure the dichroic ratio of the various dyes dissolved in E7. The cells consisted of a 1 wt% solution of dichroic dye dissolved in bulk E7 sandwiched between conducting glass substrates. A polyimide layer was spin coated on the substrates and rubbed to produce unidirectional homogeneous alignment. The thickness of the cell was controlled with 10 μm glass spacers. The edges were sealed with a five-minute epoxy.

Thermally induced phase separation was used to produce thermoplastic PDLC shutters for analysis in the IR region.⁹ Polyvinylpyrrolidone (PVP) and E7, in a 3:7 weight ratio respectively, were dissolved in chloroform. The resulting solution was poured on silicon substrates and the solvent allowed to evaporate. Glass spacers were added to control thickness. The material was then heated to 170°C forming a homogeneous solution of E7 in PVP and squeezed against a second substrate to a thickness controlled by the glass spacers. The material was cooled to room temperature. The cooling rate controlled the droplet size; the faster the rate, the smaller the droplets. The resulting shutter could be reheated and cooled at a different rate to change the droplet size.

IV. ABSORPTION MEASUREMENTS

A Perkin Elmer Lambda 4B UV/VIS double beam spectrometer with integrating sphere was used to determine the absorption of the dichroic dye containing PDLC. An identically prepared PDLC or preferentially aligned planar cell without dye was

used as a reference. For the PDLC shutter, the PDLC reference shutter corrects for light loss from back scattering and reflections in both the ON and OFF states.

Absorption values of the dyes were measured at the wavelength of maximum absorption, λ_{max} , for each dichroic cell. Measurements were made with light polarized parallel and perpendicular to the orientation of the liquid crystal in the preferentially aligned homogeneous cells. Unpolarized light was used to make absorption measurements of the ON and OFF states of a dye-containing PDLC cell.

We measured the absorbance in the IR of the aligned cells as well as the PDLCs using a Perkin-Elmer model 1600 FTIR spectrophotometer. IR polarizers were used to measure the polarization dependence of absorption for the bulk E7 samples. The absorption values in the IR were measured at the wavelength of the cyano stretch ($\lambda = 2226 \text{ cm}^{-1}$). The cyano stretch was selected for this measurement because it is well separated from other absorption bands and because of its large dichroic ratio.

The maximum absorbance and wavelength can be determined to within 0.5% and are therefore not a major source of error in these measurements. The major contribution of error in the empirically determined values of a and X arises from the uncertainty in the sample thickness. The thickness of several PDLC samples with 18 μm spacers was measured with an optical microscope. The thickness of the cells varied between 18 μm and 22 μm , which could lead to a 20% error in the reported values of a and X . We also assume the reference and sample cells have the same scattering efficiency for the determination of a . The inclusion of a dichroic dye may affect the scattering efficiency of the dye samples by changing the droplet morphology and by altering the refractive index of the droplets. In the IR measurements the film was not index matched in the ON state, leading to lower values for the fraction of liquid crystal in the droplets. We estimate the magnitude of this error.

V. RESULTS AND DISCUSSION

The polarized absorption spectra, A_{\parallel} and A_{\perp} , were measured for preferentially aligned cells containing various dichroic dyes dissolved in E7. A_{\parallel} and A_{\perp} were measured at λ_{\max} for the electric field vector of incident light parallel and perpendicular to the nematic director, respectively. Since the absorption (A) is given by Eq. (2), the measured values can be divided by the concentration of the dye (c) and path length (l) of the cell to obtain ϵ (reported as wt fraction⁻¹ μm^{-1} .) From these values, ϵ_{\parallel} of the dye can be determined from Eq. (3), and the dichroic dye ratio (R) from Eq. (4). The λ_{\max} is directly measured from the spectra. The ϵ_{\parallel} and ϵ_{\perp} values are reported in Table I for the four dyes used in this study.

The absorbance of the colored PDLC shutters in the ON and OFF states was measured at the wavelength used to determine the dye extinction coefficients. The measured value of A_{ON} is used in Eq. (8) to determine the fraction of dye (X) that remains in the droplet after phase separation. The field is then removed to measure A_{OFF} . The scattering efficiency is calculated using Eq. (7). These values are reported in Table I for the four dyes used.

The segregation of the dye in the PDLC droplets is dependent on the type of dye. The yellow (Y2), and two red (R4), and (R5) dyes are concentrated in the droplet, $X = 0.7, 1.0$, and 0.83 , respectively. However, the blue (B3) dye is concentrated in the binder, $X = 0.19$. This could be the result of the B3 dye being very soluble in the polymer, minimizing phase separation. The dye remaining in the polymer binder is randomly oriented and does not respond to an external field, reducing the achievable contrast. Therefore, it is important to choose dyes that give the maximum segregation in the liquid crystal droplets.

The calculated scattering efficiency, α , of the PDLC shutter provides insight into the effect of dichroic dyes on the contrast ratio of these films. It is clear that the dyes have a marked effect on the scattering efficiency of these films. The α values range

from 1.71 for the yellow dye (Y2) to 0.74 for the red dye (R4). The value of 0.74 for R4 is unrealistic because it indicates that the path length of light is less in the OFF state than in the ON state, a physical impossibility. The assumptions used in the derivation of Equation 7 must be carefully considered to understand this result. The absorbance in the ON and OFF states is measured relative to the reference sample which is also switched between the ON and OFF states. We assume that both the reference and sample shutters have the same OFF state scattering efficiency. If the scattering efficiency of the dyed sample is less than the undyed sample, the calculated α could be less than one. At wavelengths greater than the absorption of the R4 dye, the scattering of the sample appears to be greater than the reference, indicating an $\alpha > 1$. However, different base lines were used to determine the absorption of the R4 shutter in the ON and OFF states and should compensate for the variation in scattering. Visual inspection shows that the scattering efficiency of the R4 shutter and the undyed reference shutter are similar.

The unrealistic value for α in the R4 shutter may also be the result of changes in the droplet refractive index caused by the R4 dye. The refractive indices of the liquid crystal in the droplet will increase substantially at wavelengths absorbed by the dye. For instance, the red dye, R4, has a large ϵ_{\parallel} effectively increasing the refractive index of the liquid crystal for light polarized parallel to the droplet director; the polarization that is highly scattered. One would expect an increase in the scattering efficiency. However increased scattering by the droplets may effectively reduce the intensity of light passing through the droplet, thereby reducing the dye absorption resulting in a decrease in the calculated scattering efficiency. If the droplet size and density of these two samples are similar, the reduction in the scattering efficiency may be attributed to the change in refractive index caused by the dissolved dye. This results in a light piping phenomena where the light is highly scattered by, but does

not enter the droplets, and is not absorbed by the dye. Therefore the calculated values for α are probably less than the actual scattering efficiency.

There is considerable interest in a black PDLC shutter which has a large contrast ratio over the entire visible region for direct view displays. Black dyes usually consist of a mixture of several dichroic dyes. The fraction of the various components of dyes dissolved in the droplet must be considered when determining the amounts of dye used. A black dichroic dye was used, consisting of a mixture of the four dichroic dyes employed in this study. The ratio of the various dyes gave an optimum black mixture when used in a standard guest host cell. The absorption spectrum of the black PDLC shutter is shown in Fig. 2. The relative fraction of the various dyes dissolved in the droplets affects the color contrast. The shutter has a relatively uniform absorbance in the OFF state across the absorption bands of the four dyes. The absorption in the OFF state is independent of the dye distribution because the extinction coefficient is isotropic for dye in both the binder and the droplet. In the ON state, only dye dissolved in the droplet will align with the external field. As seen in Fig. 2, the absorbance of the blue B3 dye, $\lambda < 600$ nm, is much greater than the other dyes because a large percentage remains locked in the binder, reducing the contrast in this region. This confirms the results obtained for the single dye PDLC shutters.

The IR absorption spectra of polarized radiation, A_{\parallel} and A_{\perp} , are shown in Figure 3 for the liquid crystal E7. A_{\parallel} and A_{\perp} are measured at λ_{\max} of the CN stretch. For the CN stretch, A_{\parallel} is large ($A_{\parallel} = 1.5$) compared with A_{\perp} ($A_{\perp} = 0.26$). This is a result of the alignment of the permanent dipole moment of the CN group in the same direction as the liquid crystal (LC) director, as noted by Shin-Tson Wu.²² From the values of A_{\parallel} and A_{\perp} of the LC we calculated the IR extinction coefficients and the dichroic ratio of E7 using Eq. (2) and Eq. (4), respectively.

We also measured the IR absorbance of the PDLC shutter in the ON and OFF states at the λ_{\max} of the highly dichroic CN stretch. The IR absorption spectra of the PDLC shutters are presented in Figure 4. Eq. (8) can be used to calculate the fraction of LC confined in the droplets, X . The OFF and ON state absorption of the cyano stretch (A_{off} and A_{on} respectively) were measured relative to the background absorption resulting from substrate absorption and PDLC light scattering in this wavelength region. The values of X for a 61 μm thick PDLC, reported for different cooling rates are presented in Table II. The calculated values for X generally decrease as the cooling rate decreases, contrary to what would be expected with more time allowed for phase separation. However, Eq. (8) assumes that no light is scattered in the ON state of the shutter. This is not the case for these IR shutters because the ordinary refractive index of the liquid crystal is not well matched with that of the polymer. The magnitude of the ON state scattering will be a function of the droplet size, being most effective when Δn is on the order of the wavelength of light. The droplet size of these samples ranges from 2-20 μm depending on the cooling rate. The greater the scattering, the longer the path length of light passing through the sample and therefore the greater the measured ON state absorption and the smaller the calculated value of X . The relative light scattering of the 61 μm shutter formed by cooling at different rates can be estimated by comparing the background absorption of each shutter. Any increase in light scattering will result in an increase in the measured absorption. The value for the ON state absorption measured at 4 μm is also listed in Table II. Figure 5 shows the value of X as a function of A_{on} ($\lambda = 4 \mu\text{m}$). As predicted, the calculated value for X decreases as A_{on} ($\lambda = 4 \mu\text{m}$) increases. The actual value for X should therefore be equal to or greater than the largest calculated value of X in Table II (≥ 0.81).

The E7 PVP system was designed to modulate IR light and therefore had droplet sizes optimized for scattering in the IR. PDLC systems optimized for operation in the

visible will have much smaller droplets and negligible scattering in the IR and will therefore be more suitable for determining X from the magnitude of the cyano stretch in the ON state. We will therefore continue this research with the study of visible PDLC shutters.

VI. CONCLUSIONS

The efficiency of dichroic dyes employed in PDLC materials is investigated using UV/VIS spectroscopy. The techniques and analysis presented are a valuable tool to determine the fraction of dye dissolved in the nematic droplets and the scattering efficiency of colored PDLC shutters containing dichroic dye. A black PDLC shutter can be constructed with a large contrast ratio over the entire visible region. The determined scattering efficiency provides additional insight into the effect of dichroic dyes on the contrast of these films.

The dichroic IR absorption of the cyano stretch of the cyano biphenyl portion of the low molecular weight liquid crystal can be used in a fashion similar to a dichroic dye to calculate the fraction of liquid crystal in the droplets. This technique produces unrealistic results because of significant light scattering of the films in the ON state. However it does provide a lower limit for the fraction of liquid crystal in the droplets. More accurate determination of the segregation of the low molecular weight liquid crystal in the PDLC droplets may be achieved using films optimized for visible operation.

ACKNOWLEDGEMENTS

This research was supported by DARPA-ONR under contract #N00014-86-K-0766 and the National Center for Integrated Photonic Technology supported by DARPA under contract #MDA972-90-C-0037.

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FIGURE CAPTIONS

- FIG. 1 Schematic representation of the nematic director configuration in PDLC droplets incorporating a dichroic dye. (A) No applied electric field, and (B) droplet aligned with an applied field
- FIG. 2 The absorption spectra of an 18 μm thick black PDLC shutter containing a black dichroic dye mixture of Y2, R4, R5 and B3 in the ON and OFF states.
- Fig. 3 IR absorption spectra for the eutectic liquid crystal mixture E7 for light polarized parallel, \parallel , and perpendicular, \perp , to the liquid crystal director; for the 2-22 μm wavelength region (A) and for the 4-5 μm wavelength region (B).
- Fig. 4 ON and OFF state IR absorption spectra of a PDLC shutter formed from E7 and PVP cooled at 1°C/min for the 2-22 μm wavelength region (A) and for the 4-5 μm wavelength region, (B), and for the same shutter cooled at 2°C/min. for the 2-22 μm wavelength region (C) and for the 4-5 μm wavelength region (D).
- Fig. 5 The calculated fraction of liquid crystal in droplets in a PDLC composed of E7 and PVP as a function of the ON state scattering intensity measured at 4 μms .

TABLE I
Experimentally determined parameters and calculated values
of the scattering efficiency and percentage of dye
dissolved in droplet for various dichroic dyes.

Dye	λ_{\max}	ϵ_{\parallel}^a	ϵ_{\perp}^a	ϵ_i^a	R	A_{OFF}	A_{ON}	α	X
Y2	411	9.10	1.90	4.30	4.8	0.465	0.165	1.72	0.70
R4	500	14.20	2.16	6.18	6.6	0.290	0.110	0.74	1.00
R5	550	6.23	1.62	3.17	3.9	0.335	0.119	1.68	0.83
B3	645	9.79	0.97	3.91	10.1	0.250	0.205	1.02	0.19

a) ϵ reported in $\text{wt frac}^{-1} \mu\text{m}^{-1}$

TABLE II

ON and OFF state absorbance (A_{off} and A_{on} respectively) measured at the cyano stretch peak, the calculated fraction of liquid crystal in the droplet (X), background scattering of the PDLC at $4\mu\text{m}$ ($A_{on}(\lambda = 4\mu\text{m})$), and droplet diameter (d) as a function of cooling rate for the PVP/E7 PDLC.

	-2°C/min	-1°C/min	-0.5°C/min	-0.1°C/min
A_{off}	1.50	2.79	2.20	2.52
A_{on}	1.44	2.16	1.94	2.22
X	0.81	0.41	0.53	0.38
$A_{on}(\lambda = 4\mu\text{m})$	0.48	0.62	0.52	0.72
$d(\mu\text{m})$	8-10	12-16	18-22	20-26

ORIGINAL FIGURES

"CHARACTERIZATION OF POLYMER DISPERSED LIQUID CRYSTAL SHUTTERS BY UV AND IR ABSORPTION SPECTROSCOPY" by J. L. West and R. Ondris-Crawford, *J. Appl. Phys.*

Figure 1. (a) $\theta = 0^\circ$ (b) $\theta = 90^\circ$

